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XRF analyses for the study of painting technique and degradation on frescoes by Beato Angelico: first results

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Summary. — Beato Angelico is one of the most important Italian painters of the Renaissance period, in particular he was a master of the so-called "*buon fresco*" technique for mural paintings. A wide diagnostic campaign with X-Ray Fluorescence (XRF) analyses has been carried out on three masterworks painted by Beato Angelico in the San Marco monastery in Florence: the *Crocifissione con Santi*, the *Annunciazione* and the *Madonna delle Ombre*. The latter is painted by mixing *fresco* and *secco* techniques, which makes it of particular interest for the study of two different paintings techniques of the same artist. Then the aim of the study was focused on the characterization of the painting palette, and therefore the painting techniques, used by Beato Angelico. Moreover, the conservators were interested in the study of degradation processes and old restoration treatments. Our analyses have been carried out by means of the XRF spectrometer developed at LABEC laboratory at Istituto Nazionale di Fisica Nucleare in Florence (Italy). XRF is indeed especially suited for such a kind of study, allowing for multi-elemental, non-destructive, non-invasive analyses in a short time, with portable instruments. In this paper the first results concerning the XRF analysis are presented.

PACS 82.80.Ej – X-ray, Mössbauer, and other γ-ray spectroscopic analysis methods.
PACS 07.85.Nc – X-ray and γ-ray spectrometers.
PACS 78.70.En – X-ray emission spectra and fluorescence.

1. – Introduction

X-Ray Fluorescence (XRF) is one of the most used diagnostic techniques in the field of cultural heritage, thanks to its many favourable aspects, such as the possibility of carrying out quick (few minutes per spectrum, thanks to its high cross section), multi-elemental

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(without giving any information about molecules), non-destructive/non-invasive analyses, without any damage or sampling of the work of art. Moreover, the portability of the instrumentation allows performing *in situ* measurements, directly in the museum or in the restoration laboratory.

Revealing the elements allows discriminating the materials composing the art object, such as pigments. The main limitations of this kind of portable spectrometer, working at ambient pressure, are the lack of any information about molecules and the impossibility of revealing elements with atomic number Z lower than that of sodium. Thus XRF should be complemented by other diagnostic techniques in order to allow for a complete characterization of a work of art.

In this paper we will present the first results concerning the XRF analyses in the framework of a wide diagnostic campaign carried out on three mural paintings by Beato Angelico: *Crocifissione con Santi*, *Madonna delle Ombre*, *Annunciazione*. For our work we used the XRF spectrometer developed in Florence at LABEC laboratory (Laboratorio di Tecniche Nucleari per l'Ambiente e i Beni Culturali [1-4]) of the Italian National Institute of Nuclear Physics. It allows for the detection of elements down to sodium, thanks to the use of two X-ray tubes [5] with different anode material and continuous helium flow (see next section), which resulted to be a premium issue in our campaign. Indeed this allowed discriminating different kind of pigments and studying degradation processes, as will be discussed later.

2. – Instrumental set-up

Our instrument [5,6] is a portable XRF spectrometer with high efficiency of excitation and detection for low-Z elements. Its measuring head is based on two X-ray tubes, used separately, one for each measurement, with different anode material and a detector.

We have three anodes available: molybdenum (K_α at 17.5 keV; L_α at 2.3 keV), tungsten (L_α at 8.4 keV; L_β at 9.7 keV), and titanium (K_α at 4.5 keV); the tubes have a 125 or 75 μm thick beryllium exit window; 30 or 50 kV maximum anode voltage; 0.5 or 1.0 mA maximum anode current ("Silicon Potted" TF1000 or "Radiation Shielded" series 5000 models by Oxford Instruments). The use of two X-ray sources permits to optimize the detection of different elements, choosing the anode combination with the best excitation efficiency for the elements of interest; for example the molybdenum anode has the best excitation efficiency for elements with Z lower than that of sulphur (16) [5].

The direction of the X rays emitted by the first tube is normal to the target surface, while the second one emits at 25° with respect to this direction, the smallest possible angle in order to minimize the difference in the volumes irradiated by the two primary beams.

The detector is a silicon drift detector (Ketek GmbH, 10 mm^2 active area, 450 μm thickness, 139 eV energy resolution at Mn K_α line, 8 μm thick beryllium entrance window) located in the measuring head together with the two X-ray tubes. The detector was set to the best possible angle, taking into account all the encumbrances of all the items of the measuring head, *i.e.* 40° with respect to the normal to the sample surface.

In our spectrometer, the X-ray paths from tube to sample and from sample to detector are flooded with He, thus optimising the detection of light elements, allowing us to reveal the elements down to sodium with good sensitivity (ranging from 2 wt% to 11 ppm) [5].

The spectra have been analysed by means of WinQXas software [7].

In the measurements we used the tubes with molybdenum and tungsten anode (0° and 25°, respectively). For the *Crocifissione con Santi* we used the molybdenum tube with

Fig. 1. – *Crocifissione con Santi.*

maximum voltage of 30 kV; for the other two paintings, we used instead the molybdenum tube with maximum voltage of 50 kV in order to excite also the K-lines of tin, which is an element of interest for the study of pigments (*i.e.* lead-tin yellow) and gilding technique.

We chose the molybdenum anode to obtain the best efficiency on light elements and the tungsten one to assess the presence of sulphur, as the sulphur K_α line (~ 2.31 keV) largely overlaps the molybdenum L-line (~ 2.29 keV). In principle the Ti anode is better to detect S, but in this particular case W allows for a higher detection limit. Indeed a fresco is mainly composed of calcium carbonate, and Ti excites Ca with high efficiency thus worsening the minimum detection limit of S. Moreover, around 2.3 keV there are not only the molybdenum overlying, but also the calcium K_β escape line and the lead M lines, all of them variable in quantities, thus making the data analyses complex.

3. – The frescoes by Beato Angelico

Beato Angelico (1400–1450) is a famous Italian painter who lived in the early Renaissance period. The characteristic that distinguishes his style is the use of light, shadows and colours to create the volumetric modelling of the forms. For example, the *Madonna delle Ombre* (Madonna of the Shadows) took its name from from shadows effects painted on the wall as if they were really projected by the capitals, in accordance with the direction of a real source of light in the corridor where the painting is placed.

One of his most famous masterworks is the fresco cycle, painted between 1438 and 1445, in the monastery of San Marco in Florence, decorating all monks' cells, the corridors, the cloister and the Chapter House. The *Crocifissione con Santi*, the *Annunciazione* and the *Madonna delle Ombre* (figs. 1, 2, 3) belong to this fresco cycle.

The *Madonna delle Ombre* (fig. 3), mentioned previously is particular among the others because it was realized with an unusual painting technique for Beato Angelico, the mixing of *fresco* and *secco* techniques.

Fig. 2. – *Annunciazione.*

Fig. 3. – *Madonna delle Ombre.*

As is well known, Angelico was a great fresco painter, and then he used the "*buon fresco*" technique: in this case the painting is executed on the freshly laid plaster and the pigment is dispersed in water. It comes out to be a very durable painting since the pigment has calcium carbonate instead of an organic material as binder.

The "*secco*" technique, instead, consists in the pigment tempered in an organic medium (such as egg yolk or whole egg) and applied to the dried plaster; this allows longer times of execution, at the price of having a less durable result.

These two painting techniques make use of different types of pigments. For instance, lead-based pigments (such as lead white or minium) turn darker if employed in the *fresco* technique, which was well known since the antiquity, as attested in the Cennini's "*Libro dell'Arte*" or in [8], due to the basic environment made by plaster's calcium carbonate, thus they can be used only with the *secco* technique. Thus XRF represents a useful means to study and compare these two different painting techniques.

The few lines above should allow for understanding the interest and the motivations that suggested us to carry out a diagnostic campaign on these three masterpieces, the results of which are here briefly reported.

The diagnostic campaign has been carried out exploiting the XRF spectrometer described above.

The analyses allowed us to carry out a deep study on Beato Angelico's painting technique. We will show here just a part of the obtained results, since the large amount of data collected would need many pages to be explained. Indeed, hundreds of points were analyzed: 200 in the *Crocifissione con Santi*, 380 in the *Madonna delle Ombre* and 120 in the *Annunciazione*. Two different spectra were collected for each point of analysis (one for each X-Ray tube).

The comparison between the two "*buon fresco*" mural paintings (*Crocifissione* and *Annunciazione*) and the one mainly painted with the "*secco*" technique (*Madonna delle Ombre*) has been of great interest: in the two techniques different kinds of pigments are used and they can be easily characterized by XRF analyses. Exploiting the so-acquired info, it is possible to reverse the approach and identify the technique (*fresco* or *secco*) by the knowledge of the pigments.

The conclusions obtained following this approach can be reinforced by evaluating the absorption of calcium X-ray lines coming from the plaster, as shown in the next section **4**˙3.

4. – Results and discussion

4˙1. *Introduction to the results*. – As is well known, the study of a mural painting is a challenging task for many reasons, the most important of which are:

– The contemporary presence of plaster, pigments, degradation products, pollution and restorations carries a huge amount of information, difficult to disentangle, as it is not trivial to clearly link an element to the corresponding material. Typically, in a single measurement we get contribution from the plaster (calcium carbonate), from its aggregates (such as silicon, potassium, aluminium, iron and strontium), from degradation products (like chlorine, sulphur and lead), and from retouchings and restorations (*e.g.* zinc, titanium or lead).

– The same element may have different origins, increasing the ambiguity of the material characterization. A first example of great importance in our study: iron is

always present in the plaster, but it is also characteristic of earth pigments. Another case of interest is that of Ca and S, two elements always present in the plaster, which are also involved in sulfation, *i.e.* the formation of gypsum ($CaSO_4 \cdot H_2O$).

– In the spectral analysis, the steady presence of so many elements implies problems in the deconvolution of the X-ray lines and hence in the element identification. For example, it is nearly impossible to study sulfation in the presence of lead pigments, since the sulphur K_α line (2.31 keV) overlaps the lead M_α lines (2.34 keV) and calcium K_β escape line (2.27 keV).

4˙2. *Degradation and restoration: their influence on XRF spectra.* – Sulfation, one of the most dangerous degradation processes in mural paintings, affected also Angelico's frescoes, which in the 70's were consolidated with the "Ferroni-Dini" or "Barium" method to chemically de-sulphate the efflorescence and re-form calcium hydroxide. Thus, XRF analyses show the presence of Ba almost everywhere.

In our XRF analyses the amount of barium is erratic, even within the same painting, presumably depending on the concentration of the solution used by the restorer (Dino Dini). Actually, from the restoration journal [9], the notes written by Dino Dini during his work on the fresco, it emerges that, when using the compresses of barium hydroxide, the doses and timing of application were chosen depending on the conservation state of the areas *i.e.*: greater or lesser sulfation, more or less layers of repaintings, greater or lesser consistency of plaster, temperature and relative humidity. In particular for the *Crocifissione con Santi* the Ba concentration shows a great variability probably due to its bad and inhomogeneous conservation state.

As is well known, in the *fresco* the *giornate*, *i.e.* how much painting was done in a single day, are quite well-defined by profiles. When the restorer applies the compress, he follows these profiles and then, within a *giornata*, the concentration of the solution is the same. For this reason we divided all the collected spectra into *giornate* and calculated the average of the peak area of the barium, calculated by means of WinQXas with a Gaussian fit. The results are shown in fig. 4, where it is possible to distinguish the areas where the treatment was repeated or more concentrated.

As can be seen in fig. 4 the presence of barium is variable. In particular the gilded haloes were not treated with the *Ferroni-Dini method*. Indeed, the barium hydroxide should be used with caution for its alkalinity, which can cause softening and swelling phenomena of organic materials. The organic materials in these frescoes are found mainly in the *missione*, the preparation (and sticking) layer of gildings, made by linseed oil and little quantities of pigments. To preserve the gildings adherent to the *missione*, the restorer chose to avoid their treatment. Actually, barium was found in little amounts in small gilded decorations (as border of dresses or crosiers), most likely because it is nearly impossible to prevent the compress from touching these decorations.

In case of frescoes treated with the *Ferroni-Dini* method, as for example the *Crocifissione*, it is possible to get some evaluation about sulfation, which is one of the main causes of frescoes degradation. Indeed this treatment leaves traces of barium sulphate, which can be used as a reference for sulphur estimation.

4˙3. *Characterization of the painting palette and technique: some examples.* – The palette of Beato Angelico is not so varied because he used only poor pigments, mainly iron-based pigments (frequently named among the restorers *earths*), as suggested by his

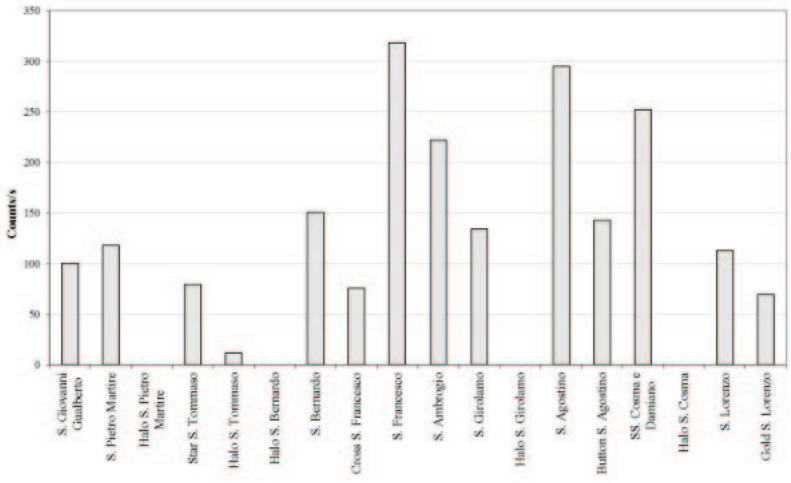

Fig. 4. – Average of barium counts in different *giornate* of the *Crocifissione Capitolare* (counts/s); each peak corresponding to a single *giornata*.

monastic philosophy. Many kinds of earths exist, from yellow to red, brown and black, depending on the quantity and quality of impurities. A high percentage of pyrolusite (MnO_2), for example, gives dark shades as in the case of umber, while the prevalence of hematite (Fe_2O_3) gives the well-known brick-red hue. Also the composition of green earths is similar, but the content of glauconite (an iron potassium phyllosilicate) and celadonite (a phyllosilicate of potassium, iron—in both oxidation states—, aluminium and hydroxide) induces different dying.

Among all the varieties of earths, described above, the by-far more abundant element is iron. The only way to discriminate different earths one from the other is to study trace elements, such as for example the low-Z ones, as K, Si, Mg, Al, the most useful in our case, and also Zn or Ti [10], and this is possible with our spectrometer. In this way it is possible to characterize the pigments and also to point out the use of mixture of earths. Two examples are reported in figs. 5 and 6.

Here different earths, mainly composed of iron, which present different colours (green, yellow and red), are compared with white areas and the plaster. In the first case (fig. 5) we compare the potassium counts with the iron ones. In the second case (fig. 6), we compare the Zn counts with the iron ones.

As shown in fig. 5, green earth can be distinguished by the larger amount of potassium; this suggests that the two green points with low K concentration in fig. 5 (in the dark green area at the end of the wing in fig. 2) correspond to an area which is not painted with a green earth but with a mixture of other earths. The dispersion of K counts is due to the variability of the K-containing minerals (glauconite and celadonite).

Figure 6 clearly shows that the yellow earth is characterized by zinc traces, not present in the other pigments. Also in this case it is possible to recognize the use of mixtures: the presence of Zn in green and red areas suggests that the yellow earth was added in order to obtain a different hue.

The same kind of pigments can be found in the *Crocifissione Capitolare* (mainly earths, St. John's White, azurite and malachite), painted with the *fresco* technique as the *Annunciazione*.

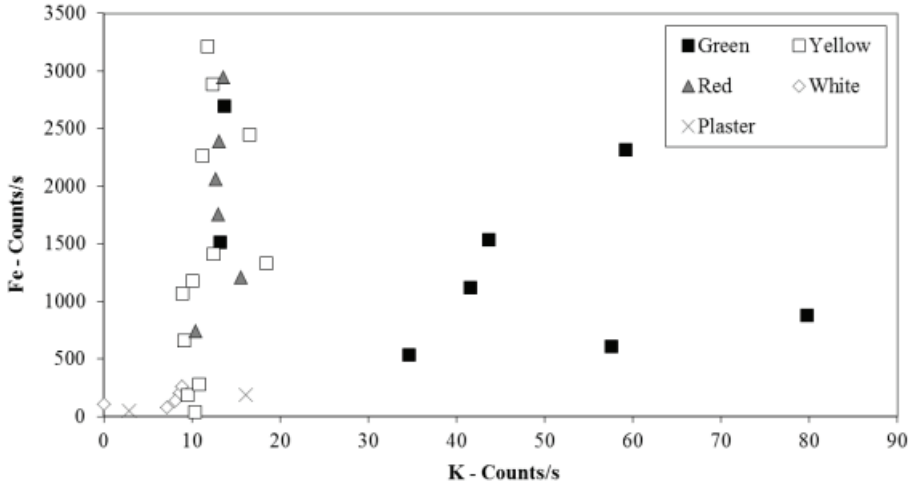

Fig. 5. – Iron *vs.* potassium counts in the *Annunciazione* (counts/s). Uncertainties are not reported because they are smaller than the points.

As mentioned before, the *Madonna delle Ombre* is mainly made with the *secco* technique. We found the characteristic elements of the *secco* technique, as mercury, lead, tin and copper, supposedly for vermillion, lead white, tin yellow and azurite/malachite, respectively.

In fig. 7 we show the comparison between two white areas painted with different pigments, the Saint John white (from the *Annunciazione*) and lead white (from the *Madonna delle Ombre*).

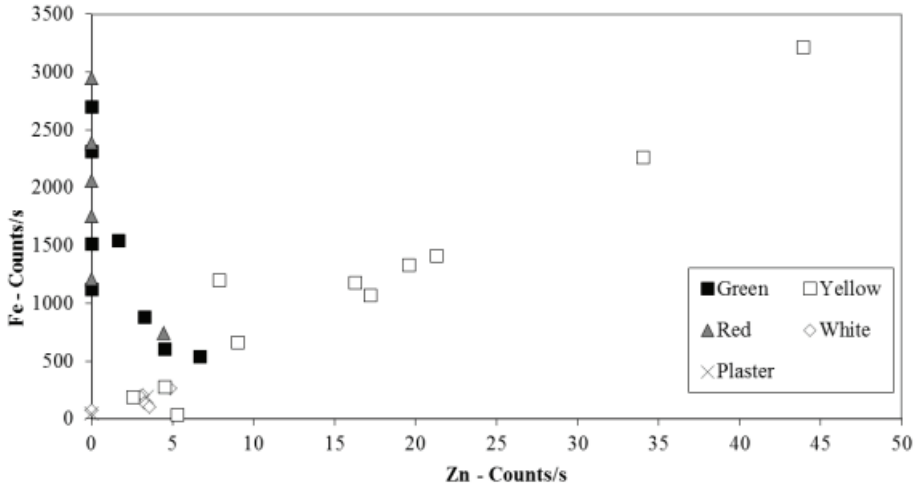

Fig. 6. – Iron *vs.* zinc counts in the *Annunciazione* (counts/s). Uncertainties are not reported because are smaller than the points.

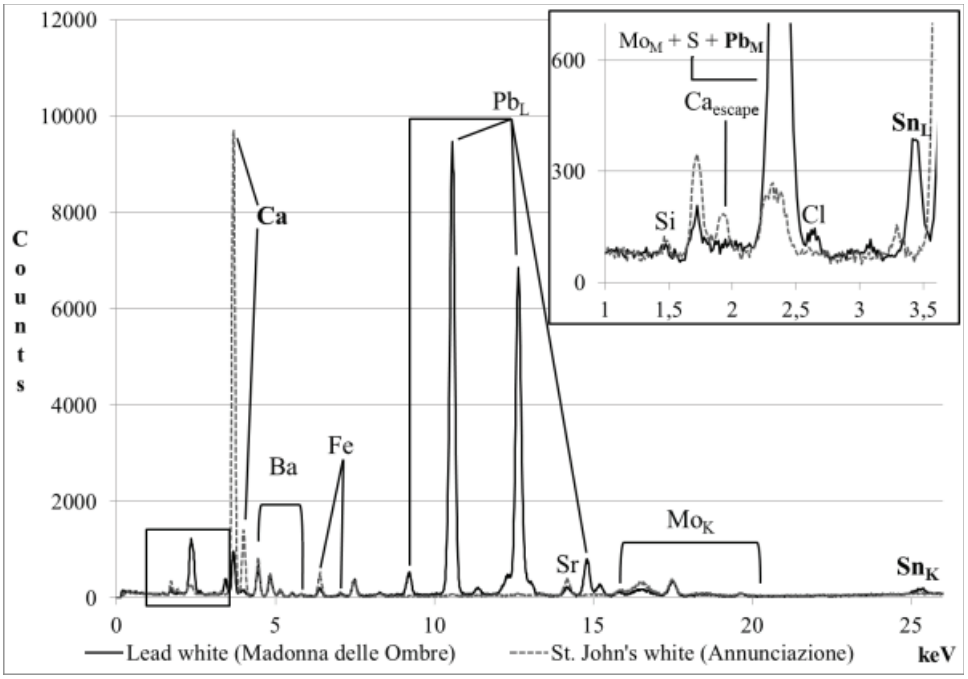

Fig. 7. – XRF spectra in two white areas of the *Madonna delle Ombre* and the *Annunciazione* (spectra, even if coming from different painting, are comparable because the experimental set-up was exactly the same—time, current and voltage).

Clearly, the most evident difference between the two spectra is the presence/absence of lead. The area of the *Annunciazione* is composed mainly of St. John's White (and maybe little amounts of earths), since we can see only the elements characteristic of the plaster. Instead, the point of analysis in the *Madonna delle Ombre* clearly shows the presence of lead, indicating the use of lead white (and some little amounts of tin yellow).

The presence of high-Z elements such as lead entails a very strong absorption of calcium, as can be seen in the spectra in fig. 7. If we consider that the *secco* technique involves mostly pigments with high-Z elements and that the medium does not contain calcium carbonate, the intensity of the Ca peak can be considered as a further indication of the use of the *fresco* or *secco* technique. In particular low calcium counts suggest high calcium absorption and thus the use of the *secco* technique.

The use of the 50 kV X-ray tube (working voltage 38 kV) permitted us to reveal also the tin K-lines, which is an impossible task with the 30 kV tube. This instrumental setup is fundamental when Ca and K are present, since the tin L-lines (3.44 keV) overlap with their K-lines (3.69 keV, 3.31 keV, respectively). This has a special importance when Sn is present in small quantities.

5. – Conclusions

The XRF campaign carried out on the Angelico's frescoes allowed us to determine the chemical composition of the materials used in these works of art and in particular to characterize the pigments and the painting techniques with a non-invasive, non-destructive

approach. In particular these achievements were possible thanks to the use of the LABEC spectrometer, a transportable, high-efficiency instrument developed for cultural-heritage studies.

The study of the remains of old restorations allowed us to evaluate the old conservation state and therefore helped us in the study of the present conservation state of the painting.

XRF analyses allowed us to discriminate among different kinds of pigments, in particular for the discrimination of different varieties of earths and also their mixtures, by means of the study of trace elements like Zn and low-Z elements as K. Moreover the study of the pigments used in the two *fresco* and *secco* techniques allowed for the study of the two different painting techniques used by Beato Angelico.

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